

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 537 609 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
14.08.1996 Bulletin 1996/33

(51) Int. Cl.⁶: **C07C 2/32**, B01J 31/18,
B01J 31/22, B01J 101/30,
B01J 103/48

(21) Application number: 92117109.6

(22) Date of filing: 07.10.1992

(54) Ethylene oligomerization

Ethylen Oligomerisierung
Oligomérisation d'éthylène

(84) Designated Contracting States:
BE DE FR GB IT

(30) Priority: 16.10.1991 US 777137

(43) Date of publication of application:
21.04.1993 Bulletin 1993/16

(73) Proprietor: **ALBEMARLE CORPORATION**
Richmond, Virginia 23219 (US)

(72) Inventor: **Wu, Feng-Jung**
Baton Rouge, Louisiana 70801 (US)

(74) Representative: **Sandmaier, Kurt, Dr. Dr. et al**
Patentanwälte
Schwabe, Sandmaier, Marx
Stuntzstrasse 16
81677 München (DE)

(56) References cited:
EP-A- 0 237 079

Remarks:

The file contains technical information submitted
after the application was filed and not included in
this specification

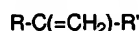
Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 537 609 B1

Description

This invention relates generally to the oligomerization/trimerization of ethylene and more specifically to the preparation of high quality linear α -olefins from ethylene using a catalyst which includes an aluminoxane and a chromium complex containing a coordinating polydentate ligand, such as a 1,4,7-triazacyclononane derivative.

The preparation of linear, C_4 to C_{30} α -olefin mixtures by ethylene chain growth process using triethylaluminum followed by ethylene displacement is well known. The olefin type produced is mainly α -olefins, i.e., $R-CH=CH_2$, where R is an aliphatic hydrocarbon group, but the product also contains lesser amounts of internal olefins, i.e., $R-CH=CH-R$, where R is an aliphatic hydrocarbon group, and vinylidene olefins, i.e.,



where R and R' are aliphatic hydrocarbon groups. When practiced to produce olefin mixtures containing up to 12 carbon atoms, the mixtures are predominantly, i.e., 80 mole percent or more α -olefins. However when practiced to produce higher olefins, e.g., containing 14 or more carbon atoms, the amount of internal olefins, and especially vinylidene olefins, increases sharply such that in the C_{16-18} olefin range the olefin mixture will contain 20 to 55 mole percent vinylidene olefins and 5 to 20 mole percent internal olefins. In some uses the internal and vinylidene olefin content of the olefin mixtures is not detrimental. However, it is known that vinylidene olefins are readily sulfonated but the detergency and wetting performance of the derived sulfonates are inferior to those of sulfonates based on the corresponding linear α -olefins. Similar reservations apply to sulfonates of internal olefins. Also, as is well known, the reaction of α -olefins with HBr can lead to the 1-bromo or to the 2-bromo derivative depending on the reaction conditions. In the detergent industry, the 1-bromo derivatives are of more interest as they provide a route to dialkylamines and hence to amine oxides and quaternary amines. It is reported that any internal olefins present (which in principle are more reactive than α -olefins) will react to form internal bromides. Similarly, vinylidene olefins would rapidly add HBr. Hence, an impure α -olefin would lead ultimately to a tertiary amine containing a wide range of impurities. Thus, with products obtained by ethylene chain growth, a need often exists to separate internal and vinylidene olefins from mixtures containing vinyl, vinylidene and internal olefins which mixtures cannot be readily separated by distillation.

EP-A-0 237 079 discloses a process for the trimerization of an olefin selected from ethylene, propylene, 1-butene and mixtures thereof comprising passing the olefin in contact with a catalyst comprising the reaction product of

- (i) a chromium compound of the formula CrX_n wherein X is an inorganic or organic radical and n is an integer from 1 to 6,
- (ii) a hydrocarbyl aluminum hydrolized with 0.8 to 1.1 moles of water per mole of aluminum compound and
- (iii) a ligand selected from hydrocarbyl isonitriles, amines and ethers wherein the aluminum to chromium mole ratio is in the range of up to 200 : 1 and the ligand to chromium mole ratio is in the range of up to about 100 : 1.

Another problem with the chain growth process is that the commercial demand for 1-hexene often exceeds the amount which is obtainable from even the most favorable chain growth product distribution.

An ethylene oligomerization process has now been found which produces high quality α -olefins which are unexpectedly enriched in 1-hexene.

In accordance with this invention there is provided A process for preparing α -olefins, said process comprising oligomerizing ethylene in the presence of a catalyst comprising (a) a chromium complex containing a coordinating polydentate ligand and having the formula $LCrX_3$ or $LCrX_2$ wherein L is a cyclic polyamine ligand represented by $A-NR-B$, where R is a C_1 to C_{10} alkyl or a C_6 to C_{20} aryl group, A represents the ring size and is an integer from 9 to 18 and B represents the number of N atoms in the ring and is an integer from 3 to 6, or a poly(pyrazolyl)borate anion of the type $RB(P_2)_3$ where R is a C_1 to C_{10} alkyl group and P_2 is a pyrazole or a substituted pyrazole and X represents anions which can be the same or different and (b) an aluminoxane in an organic solvent at a temperature of from 35°C to 200°C and at an ethylene pressure of from atmospheric to 20.8 MPa (3000 psig).

Also provided is A catalyst comprising (a) a chromium complex containing a coordinating polydentate ligand and having the formula $LCrX_3$ or $LCrX_2$ wherein L is a cyclic polyamine ligand represented by $A-NR-B$, where R is a C_1 to C_{10} alkyl or a C_6 to C_{20} aryl group, A represents the ring size and is an integer from 9 to 18 and B represents the number of N atoms in the ring and is an integer from 3 to 6 or a poly(pyrazolyl)borate anion of the type $RB(P_2)_3$ where R is a C_1 to C_{10} alkyl group and P_2 is a pyrazole or a substituted pyrazole and X represents anions which can be the same or different and (b) an aluminoxane.

Aluminoxanes for use in the process of the invention can be prepared as known in the art by reacting water or water containing materials with trialkylaluminum compounds in proportions of from 0.5 to 1.2 equivalents of water and, preferably, 0.8 to 1.0 equivalent of water per equivalent of trialkylaluminum. For example, Manyik et al U.S. 3,300,458 pre-

pare alkylaluminoxane by passing a hydrocarbon solvent through water to form a wet hydrocarbon solvent and mixing the wet hydrocarbon solvent with an alkyl aluminum/hydrocarbon solvent mixture in a conduit.

Schoenthal et al. U.S. 4,730,071 show the preparation of methylaluminoxane by dispersing water in toluene using an ultrasonic bath and then adding a toluene solution of trimethyl aluminum to the dispersion. Schoenthal et al. U.S. 4,730,072 is similar except it uses a high speed, high shear-inducing impeller to form the water dispersion.

Edward et al. U.S. 4,772,736 describe an aluminoxane process in which water is introduced below the surface of a solution of hydrocarbyl aluminum adjacent to a stirrer which serves to immediately disperse the water in the hydrocarbon solution.

The preparation of alkyl aluminoxanes from R_2AlOLi formed by reacting AlR_3 and anhydrous lithium hydroxide, and R_2AlCl has been reported in the literature, for example, Ueyama et al., *Inorganic Chemistry*, **12**, No. 10, 2218 (1973) and Aoyazi et al., *Inorganic chemistry*, **12**, No. 11, 2702 (1973).

Sinn et al. U.S. 4,404,344 prepare methylaluminoxane by adding trimethyl aluminum to a slurry of $CuSO_4 \cdot 5H_2O$ in toluene. Introducing water as a metal hydrate controls its reactivity with the trimethyl aluminum. Kaminsky et al. U.S. 4,544,762 is similar except it uses an aluminum sulfate salt hydrate to supply the water. Likewise, Welborn et al. U.S. 4,665,208 describe the use of other metal salt hydrates such as $FeSO_4 \cdot 7H_2O$ as a water source in preparing aluminoxane.

Hydrocarbylaluminoxanes may exist in the form of linear or cyclic polymers with the simplest compounds being a tetraalkylaluminoxane such as tetraethylaluminoxane, $(C_2H_5)_2AlOAl(C_2H_5)_2$. The compounds preferred for use are prepared from hydrocarbylaluminum compounds in which the alkyl groups contain an even number of carbon atoms, e.g., 2, 4, 6, 8, or 10, etc. Using methylaluminoxane can result in α -olefin mixtures which contain odd carbon number α -olefin impurities and tends to produce products having longer chain lengths. Preferred aluminoxanes are prepared from trialkyl aluminum compounds such as triethyl aluminum, triisobutyl aluminum, tri-n-hexyl aluminum, and tri-octyl aluminum. Of these, the more preferred are the compounds having C_6 or higher alkyl groups which have better solubility in the hydrocarbon solvent reaction medium. The aluminoxanes used to form the catalyst are preferably contained in organic solvents in concentrations of from 0.3 to 30 weight percent of total solvent plus aluminoxane.

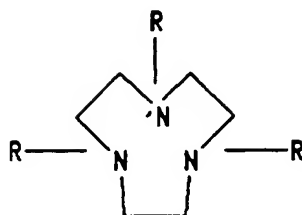
A trialkylaluminum compound can also be included in the catalyst (0.1 to 1.0 mole per mole of aluminoxane).

The chromium complexes which, upon mixing with an aluminoxane, catalyze ethylene oligomerization and trimerization in accordance with the process of the invention are represented by the formula: $LCrX_3$ or $LCrX_2$, where L is a coordinating polydentate ligand and X represents anions which can be the same or different.

By a coordinating ligand is meant that the ligand sterically encumbers the chromium atom to such an extent that the rate of chain propagation is decreased so that oligomerization rather than polymerization occurs. For example, ligands which occupy three neighboring coordination sites about an octahedral chromium atom. The coordinating polydentate ligands used are cyclic polyamine ligands which are represented by the abbreviation: A-NR-B, where A represents the ring size and is an integer of 9 to 18, B represents the number of N atoms in the ring and is an integer of 3 to 6, and R is a C_1 to C_{10} alkyl group such as a methyl, ethyl, propyl, butyl, pentyl, hexyl or higher alkyl group or a C_6 to C_{20} aromatic group such as benzyl. The abbreviations, such as 9-NR-3, 10-NR-3, or 12-NR-4, used for the amine ligands correspond to those used for crown ethers because they are their nitrogen analogues. For example, 9-NR-3 denotes a nine membered ring with 3 nitrogens. The most preferred coordinating polydentate ligands are facially coordinating tridentate ligands such as 9-NMe-3. Such sterically demanding ligands permit both ethylene oligomerization and trimerization while inhibiting ethylene polymerization. Other suitable facially coordinating tridentate ligands include poly-(pyrazolyl) borates of the type: $RB(P_2)_3$ anions, where R is as defined above and P_2 is pyrazole or a substituted pyrazole such as 3,5-dimethyl pyrazole (see P. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115-210. By polydentate is meant that the ligand contains multiple donor atoms for coordination with chromium.

Examples of suitable anions, X, include, but are not limited to, halides (Cl^- , Br^- , I^- , F^-), alkoxides (OR^-), carboxylates (O_2CR^-), or Oxo(O^{2-}). These anions are initially the anion portion of the chromium compounds used to make the complex. The chromium in the compounds is initially in the oxidation state of 0 to VI and is preferably in the oxidation state of II, III or IV. Suitable chromium compounds are those which will provide the complex with active catalytic species for the oligomerization/trimerization reaction under the reaction conditions. For example: those which provide chromium complexes such as $(9-NMe-3)CrCl_3$, $HB(3,5-Me_2P)_3CrCl_3$, $[(14-NH-4)CrCl_2]Cl$ (or oxo-bridged dimer such as $[LCrCl_2]_2O$, where L is a tetradentate ligand), $(9-NMe-3)Cr(OR)_3$, $(9-NMe-3)Cr(O_2CR)_3$, and $(9-NMe-3)CrO_3$.

Preferred ligands for complexing with the chromium compounds are the alkyl substituted 1,4,7-triazacyclononanes. For example, 1,4,7-trialkyl 1,4,7-triazanones which have the structure:



where each R can be the same or different C₁ to C₁₀ alkyl or C₆ to C₂₀ aromatic groups. All especially preferred ligand is 1,4,7-trimethyl-1,4,7-triazacyclononane. This ligand is commercially available.

The chromium complexes can be prepared according to procedures set forth in the literature. For example (9-NMe-3)CrCl₃, where Me is methyl, as per K. Wiegart et al., *Inorg. Chem.* 1982, **21**, 3086 and (9-NMe-3)CrBr₃ as per P. Chaudhuri et al., *Inorg. Chem.* 1987, **26**, 3302.

The chromium complex and aluminoxane are combined in proportions to provide Al/Cr molar ratios of from 1:1 to 10,000 to 1 and, preferably, from 5:1 to 500 to 1. For longer catalyst life, the catalyst components are combined in situ under ethylene pressure just prior to use in the oligomerization/trimerization reaction. Amounts of 0.001 mmole or more of chromium catalyst are effective to catalyze the reaction.

The reaction is carried out in an inert solvent. Any inert solvent can be used. The preferred solvents are aliphatic and aromatic hydrocarbons and halogenated hydrocarbons such as, for example, toluene, xylene, ethylbenzene, cumene, mesitylene, heptane, cyclohexane, methylcyclohexane, 1-hexene, 1-octene, chlorobenzene, and dichlorobenzene. The amount of solvent is not particularly critical and generally ranges from 50 to 99 wt.percent of the initial reaction mixture.

Reaction temperatures and pressures affect the chain length of the product and are selected to optimize the amount of the desired products. Higher temperatures provide lower carbon number products and higher ethylene pressures favor the production of longer chain length products including some polyethylene. Reaction temperatures range from 35° to 200°C and, preferably, 95° to 150°C. Ethylene pressures range from atmospheric to 20.8 MPa (3000 psig) and, preferably 0.79 - 10.35 MPa (100-1500 psig.)

The process produces chain growth products which are a Schulz-Flory distribution of C₄-C₃₀ α-olefins except that 1-hexene is selectively enriched which provides an economically attractive means of producing this α-olefin which is a widely used comonomer in linear low density polyethylene production. The process has the further advantage of producing α-olefin products without the formation of significant amounts of vinylidenes or polyethylene which tends to deactivate the catalyst and cause other operational problems.

Besides oligomerizing ethylene, co-oligomers of ethylene with minor amounts of other α-olefins such as propylene or butene-1 can also be prepared.

The invention is further illustrated by, but is not intended to be limited, to the following examples.

All operations involving the use of catalyst components were conducted under an inert atmosphere. Heptane, chlorobenzene, and toluene were freshly distilled under nitrogen from calcium hydride, phosphorus pentoxide, and sodium benzophenone ketyl, respectively. Triisobutylaluminum, trihexylaluminum and methylaluminoxane were commercial products of Ethyl Corporation and were used as received. 1,4,7-trimethyl-1,4,7-triazacyclononane (9-NMe-3), 1,4,7-triazacyclononane (9-NH-3), and 1,4,7-trithiacyclononane (9-S-3) were purchased from Aldrich and used as received. (9-NMe-3)CrCl₃, (9-NMe-3)CrBr₃, (9-NH-3)Cr(CO)₃, and CrCl₃ · 3Pyridine were prepared according to literature procedures. Ethylene is polymer grade from Matheson and was used without further purification.

Preparation of n-Hexylaluminoxane, NHAO

The reaction was carried out in an 1 L three-necked round-bottom Morton flask equipped with a mechanical stirrer, a thermometer, and a rubber septum. To this flask containing a solution of trihexylaluminum (59.3 g, 0.200mol) in toluene (129 g) with vigorous stirring, was added distilled water (3.10 ml, H₂O/Al molar ratio = 0.86) using a syringe pump over a period of 45 minutes. The temperature was maintained at 10-15°C by applying an ice bath. After water addition was complete, the solution was stirred at 50°C for one additional hour and then allowed to air cool slowly. Since there was little or no insoluble material formed, a quantitative yield is assumed and Al wt percent is calculated to be 2.87 % which agrees well with analysis. The solution was transferred and stored under inert atmosphere for subsequent reac-

tions. The NHAO solution thus obtained remained active after up to 6 months of its preparation. The isobutylaluminum-oxane solutions (IBAO) were prepared analogously except in n-heptane instead of in toluene.

Ethylene Oligomerization (Examples 1 - 15 and Comparisons 1-4)

All reactions in Table I, unless otherwise noted, were carried out using the following exemplary procedures in which the specific process parameters and results described are those of Example 4.

Into a 300 ml Parr reactor equipped with a stirring shaft, a thermocouple, a dip tube and a cooling coil was charged in a drybox a mixture of (9-NMe-3)CrCl₃ (33 mg, 0.1 mmol), pentadecene (0.36 g, as internal reference for GC analysis), and toluene (100 ml). Into a 75 ml charging-bomb, which was connected to the dip tube of the Parr reactor at one end, was charged the above-prepared NHAO in toluene (7.53 g solution, 8.0 mmol Al). After sealing, the charging-bomb-connected reactor was transferred out of the drybox, connected to an ethylene cylinder at the other end of the charging-bomb, and heated to 105°C. Catalyst component mixing was carried out by pressing the NHAO solution in the charging-bomb into the reactor using ethylene gas, and in the meantime, the reactor was pressurized. The ethylene oligomerization reaction proceeded immediately at 105°C under 3.03 MPa (425 psig) ethylene pressure and was continued for 30 minutes with constant ethylene feeding to maintain the pressure. The reaction was then terminated by pressing an aqueous solution of potassium hydroxide into the reactor to deactivate the catalyst. Ethylene consumption was 32 grams as determined by weighing the ethylene cylinder. The reactor was then cooled to <10°C, vented and a sample was withdrawn for capillary GC analysis which showed a product distribution (weight percent) as follows: C₄:9.4%, C₆:39.3%, C₈:10.0%, C₁₀:8.5%, C₁₂:6.9%, C₁₄:6.0%, C₁₆:5.0%, C₁₈:4.0%, C₂₀₊:10.9%. The weight of C₈-C₁₈ fractions was used to calculate Schulz-Flory distribution coefficient β (=0.41) by fitting the following simplified Schulz-Flory equation:

$$X_p = \beta / (1 + \beta)^p$$

where X_p = mole fraction of C_{2p+2} olefin

The weight of C₄ and C₂₀₊ fractions was then obtained by extrapolation from Schulz-Flory distribution. The weight of C₆ fraction was calculated using measured response factor which was obtained from mimic experiments to simulate the operational loss. The selectivity of linear α-olefin was 85-95% with major impurities being paraffins, internal olefins and cyclic olefins.

Table I
Ethylene Oligomerization/Trimerization Reactions Catalyzed by $ICrX_3$ /Aluminoxane System

EXAMPLE NO.	CATALYST ¹ mmol	P (psig) MPa	T °C	SOLVENT ²	TIME Min.	ACTIVITY mol/mpl Cr/h ³	β^3	C ₄ wt. % ⁴	
								Found	Calcd.
Effects of Temperature and Pressure									
1	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.067 5.8	(615) 5.72	130	T	30	18,214	0.8-1.1	46	7
2	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.067 5.8	(640) 5.89	115	T	30	31,071	0.39	30	10
3	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.05 4.0	(540) 3.82	115	T	30	21,429	0.56	46	12
4	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.1 8.0	(425) 3.03	105	T	30	22,857	0.41	39	10
5	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.067 6.0	(230) 1.69	95	T	30	17,143	0.30	37	6
Comparison 1	(9-NMe-3)CrCl ₃ /IBAO(0.88) 0.1 6.0	(540) 3.82	30	CB	30	1,948	0 (polymer only)		
Type of Aluminoxanes									
6	(9-NMe-3)CrCl ₃ /IBAO(0.94) 0.1 10.0	(440) 3.13	105	T	30	8,571	0.40	40	9
7	(9-NMe-3)CrCl ₃ /IBAO(0.94)/TNIA 0.1 8.0 2.0	(440) 3.13	105	T	30	18,571	0.42	36	10
8	(9-NMe-3)CrCl ₃ /IBAO(0.94)/TEA 0.1 6.0 1.5	(540) 3.82	115	CB	30	7,929	0.44	36	9
9	(9-NMe-3)CrCl ₃ /MAO(0.50) 0.1 6.0	(550) 3.89	115	CB	30	1,714	0.1-0.3	31	-

Table I - (Continued)

EX. NO.	CATALYST ¹ mmol	P (psig)	T °C	SOLVENT ²	TIME Min.	ACTIVITY mol/mq ¹ Cr/h ³	β^3	C ₀ wt. %	
								Found	Calcd.
Effects of Solvent									
10	(9-NMe-3)CrCl ₃ /IBAO(0.94)/TNIA 0.1 8.0 2.0	(450) 3.20	115	CB	30	8,571	0.49	44	11
11	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.1 8.0	(560) 3.16	115	H	30	6,429	0.66	52	16
12	(9-NMe-3)CrCl ₃ /NIAO(0.86) 0.067 5.8	(820) 5.15	115	MCH	30	20,256	0.50	35	12
Type of Chromium Compound									
Comparison 2	(9-NH-3)CrCl ₃ /NIAO(0.86) 0.1 10.0	(430) 3.06	105	T	5	69,231	0 (polymer only)		
Comparison 3	CrCl ₃ ·3Py/NIAO(0.86) 0.1 8.0	(420) 3.00	105	T	30	12,143	0 (polymer only)		
13	(9-NMe-3)CrBr ₃ /IBAO(0.94)/TEA 0.1 6.0 1.5	(505) 3.52	115	CB	30	3,571	0.2-0.4	26	-
Comparison 4	(9-S-3)CrCl ₃ /IBAO(0.83) 0.1 6.0	(520) 3.62	115	CB	60	low (some polymer produced)			
Manner of Catalyst Component Mixing									
14	(9-NMe-3)CrCl ₃ /IBAO(0.94)/TNIA 0.1 8.0 2.0	(430) 3.06	115	T	50	3,857	0.69	43	12
15	(9-NMe-3)CrCl ₃ /NIAO(0.94)/TNIA 0.1 8.0 2.0	(440) 3.13	115	T	30	10,714	0.85	49	15

Table I - Page 3

1. 9-NHe-3 = 1,4,7-trimethyl-1,4,7-triazacyclononane, 9-NH-3 = 1,4,7-triazacyclononane.
 9-S-3 = 1,4,7-trithiacyclononane.
 NHAO = n-hexylaluminumoxane, IBAO = isobutylaluminumoxane.
 The number in the parentheses represents the hydrolysis ratios.
 TEA = triethylaluminum, THIA = tri-n-hexylaluminum.
 PY = pyridine
 2. T = toluene, CB = chlorobenzene, H = heptane, MCl = methylcyclohexane.
 3. β : Schulz-Flory distribution coefficient.
 Some reactions gave product distribution not following the Schulz-Flory rule. In those cases, a range of β was used to represent the product distribution between C_4 and C_{10} (usually, β decreases as chain length becomes longer and, as a result, C_4 wt. % (calcd) could not be calculated.
 4. C_4 wt. % (found) = amount of C_4 found/ethylene consumption.
 C_4 wt. % (calcd) = amount of C_4 calculated from the Schulz-Flory equation/ethylene consumption.
 5. Moles of ethylene per mole of chromium per hour.
- For comparison with Example 15, Example 14 was carried out with a time lag of about 20 minutes between catalyst component mixing at room temperature (in the absence of ethylene) and ethylene reaction at 115°C.

Comparison 1 shows that for any given system at too low a temperature, only polymer results. Comparisons 2-4 show the need for alkyl substitution of the heteroatoms to provide an effective coordinating polydentate ligand in the chromium complex which provides oligomerization rather than polymerization. Oligomerization is believed to result from the difficult access of ethylene to the active catalyst sites which is afforded by such polydentate ligands. The amount of

C₆ actually produced (trimerization) is, as shown by the last two columns in Table I, much greater than what is predicted by calculation. Also, the process of the invention favors the production of lower carbon number products compared to the prior art chain growth process on aluminum alkyls which provides products with a Poisson distribution of carbon numbers. When the prior art process is operated to peak the Poisson distribution at the lower carbon numbers (C₆-C₈) the products still include large amounts of the long chain olefin (C₁₀₊) and such products contain significant amounts of undesirable vinylidene isomers of such long chain olefins.

Claims

1. A process for preparing α -olefins, said process comprising oligomerizing ethylene in the presence of a catalyst comprising (a) a chromium complex containing a coordinating polydentate ligand and having the formula LCrX_3 or LCrX_2 wherein L is a cyclic polyamine ligand represented by A-NR-B, where R is a C₁ to C₁₀ alkyl or a C₆ to C₂₀ aryl group, A represents the ring size and is an integer from 9 to 18 and B represents the number of N atoms in the ring and is an integer from 3 to 6, or a poly(pyrazolyl)borate anion of the type $\text{RB}(\text{P}_2)_3$ where R is a C₁ to C₁₀ alkyl group and P₂ is a pyrazole or a substituted pyrazole and X represents anions which can be the same or different and (b) an aluminoxane in an organic solvent at a temperature of from 35°C to 200°C and at an ethylene pressure of from atmospheric to 20.8 MPa (3000 psig).
2. The process of claim 1 wherein said ligand is a 1,4,7-trialkyl-1,4,7-triazacyclononane.
3. The process of claim 1 wherein the catalyst is formed by combining the chromium complex and the aluminoxane in an ethylene atmosphere.
4. The process of any of the preceding claims wherein the aluminoxane is a tetraalkylaluminoxane in which the alkyl groups each contain an even number of carbon atoms.
5. A catalyst comprising (a) a chromium complex containing a coordinating polydentate ligand and having the formula LCrX_3 or LCrX_2 wherein L is a cyclic polyamine ligand represented by A-NR-B, where R is a C₁ to C₁₀ alkyl or a C₆ to C₂₀ aryl group, A represents the ring size and is an integer from 9 to 18 and B represents the number of N atoms in the ring and is an integer from 3 to 6, or a poly(pyrazolyl)borate anion of the type $\text{RB}(\text{P}_2)_3$ where R is a C₁ to C₁₀ alkyl group and P₂ is a pyrazole or a substituted pyrazole and X represents anions which can be the same or different and (b) an aluminoxane.
6. The catalyst of claim 5 wherein said ligand is a 1,4,7-trialkyl-1,4,7-triazacyclononane.
7. The catalyst of claim 5 or 6 wherein the aluminoxane is a tetraalkylaluminoxane in which the alkyl groups each contain an even number of carbon atoms.

Patentansprüche

1. Verfahren zur Herstellung von α -Olefinen, bei dem man Ethylen in Gegenwart eines Katalysators mit folgenden Bestandteilen:
 - (a) einem Chromkomplex, der einen koordinierenden Polydentatliganden enthält und der Formel LCrX_3 oder LCrX_2 entspricht, in der L ein durch A-NR-B dargestellter cyclischer Polyaminligand ist, wobei R eine C₁ bis C₁₀-Alkyl- oder eine C₆ bis C₂₀-Arylgruppe ist, A die Ringgröße angibt und eine ganze Zahl von 9 bis 18 ist und B die Anzahl von N-Atomen im Ring angibt und eine ganze Zahl von 3 bis 6 ist, oder ein Poly(pyrazolyl)boratanion des Typs $\text{RB}(\text{P}_2)_3$ ist, wobei R eine C₁ bis C₁₀-Alkylgruppe ist und P₂ ein Pyrazol oder ein substituiertes Pyrazol bedeutet und X Anionen darstellt, die gleich oder verschieden sein können, und
 - (b) einem Aluminoxan
 in einem organischen Lösungsmittel bei einer Temperatur von 35 bis 200°C und einem Ethylen-Druck von atmosphärischem Druck bis 20,8 MPa (3000 psig) oligomerisiert.
2. Verfahren nach Anspruch 1, bei dem der Ligand ein 1,4,7-Trialkyl-1,4,7-triazacyclononan ist.
3. Verfahren nach Anspruch 1, bei dem der Katalysator durch Kombinieren des Chromkomplexes und des Aluminoxans in einer Ethylenatmosphäre hergestellt wird.

4. Verfahren nach einem der vorstehenden Ansprüche, bei dem das Aluminoxan ein Tetraalkylaluminoxan ist, in dem die Alkylgruppen jeweils eine gerade Zahl von Kohlenstoffatomen enthalten.

5. Katalysator mit

(a) einem Chromkomplex, der einen koordinierenden Polydentatliganden enthält und der Formel $LCrX_3$ oder $LCrX_2$ entspricht, in der L ein durch A-NR-B dargestellter cyclischer Polyaminligand ist, wobei R eine C_1 bis C_{10} -Alkyl- oder eine C_6 bis C_{20} -Arylgruppe ist, A die Ringgröße angibt und eine ganze Zahl von 9 bis 18 ist und B die Anzahl von N-Atomen im Ring angibt und eine ganze Zahl von 3 bis 6 ist, oder ein Poly(pyrazolyl)boratanion des Typs $RB(P_z)_3$ ist, wobei R eine C_1 bis C_{10} -Alkylgruppe ist und P_z ein Pyrazol oder ein substituiertes Pyrazol bedeutet und X Anionen darstellt, die gleich oder verschieden sein können, und

(b) einem Aluminoxan.

6. Katalysator nach Anspruch 5, bei dem der Ligand ein 1,4,7-Trialkyl-1,4,7-triazacyclononan ist.

7. Katalysator nach Anspruch 5 oder 6, bei dem das Aluminoxan ein Tetraalkylaluminoxan ist, in dem die Alkylgruppen jeweils eine gerade Zahl von Kohlenstoffatomen enthalten.

Revendications

1. Procédé de production d' α -oléfines, qui comprend l'oligomérisation d'éthylène en présence d'un catalyseur comprenant (a) un complexe de chrome contenant un ligand polydenté de coordination et répondant à la formule $LCrX_3$ ou $LCrX_2$ dans laquelle L est un ligand polyaminé cyclique représenté par la formule A-NR-B, dans laquelle R est un groupe alkyle en C_1 à C_{10} ou un groupe aryle en C_6 à C_{20} , A représente la grandeur du noyau et est un nombre entier de 9 à 18 et B représente le nombre d'atomes d'azote dans le noyau et est un nombre entier de 3 à 6, ou un anion poly(pyrazolyl)borate du type $RB(P_z)_3$ où R est un groupe alkyle en C_1 à C_{10} et P_z est un pyrazole ou un pyrazole substitué et X représente des anions qui peuvent être identiques ou différents, et (b) un aluminoxane, dans un solvant organique à une température de 35°C à 200°C et à une pression d'éthylène allant de la pression atmosphérique à une pression manométrique de 20,8 MPa (3000 lb/in²).

2. Procédé suivant la revendication 1, dans lequel le ligand est le 1,4,7-trialkyl-1,4,7-triazacyclononane.

3. Procédé suivant la revendication 1, dans lequel le catalyseur est formé par réunion du complexe de chrome et de l'aluminoxane dans une atmosphère d'éthylène.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'aluminoxane est un tétraalkylaluminoxane dont les groupes alkyle contiennent chacun un nombre pair d'atomes de carbone.

5. Catalyseur comprenant (a) un complexe de chrome contenant un ligand polydenté de coordination et répondant à la formule $LCrX_3$ ou $LCrX_2$ dans laquelle L est un ligand polyaminé cyclique représenté par la formule A-NR-B, dans laquelle R est un groupe alkyle en C_1 à C_{10} ou un groupe aryle en C_6 à C_{20} , A représente la grandeur du noyau et est un nombre entier de 9 à 18 et B représente le nombre d'atomes d'azote dans le noyau et est un nombre entier de 3 à 6, ou un anion poly(pyrazolyl)borate du type $RB(P_z)_3$ dans laquelle R est un groupe alkyle en C_1 à C_{10} et P_z est un pyrazole ou un pyrazole substitué et X représente des anions qui peuvent être identiques ou différents, et (b) un aluminoxane.

6. Catalyseur suivant la revendication 5, dans lequel le ligand est un 1,4,7-trialkyl-1,4,7-triazacyclononane.

7. Catalyseur suivant la revendication 5 ou 6, dans lequel l'aluminoxane est un tétraalkylaluminoxane dont les groupes alkyle contiennent chacun un nombre pair d'atomes de carbone.